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LITERATURE REVIEW AND EVALUATION OF  
SOLID SORBENTS FOR WATER SAMPLING OF EXPLOSIVES

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## SUMMARY

Literature on a wide range of solid sorbent materials has been reviewed and evaluated to find sorbents which could be used for analysis of trace quantities of explosives in water. In the field, explosives would be concentrated by sorption onto a cartridge of sorbent material, then desorbed for analysis in the laboratory. Desirable characteristics in a sorbent are therefore quantitative adsorption of explosives to be analyzed from water and effective desorption of the explosives for analysis.

A number of types of solid sorbents were evaluated, including styrene divinylbenzene resins, acrylic esters, vinyl pyrrolidones, vinyl pyridines, acrylonitrile divinylbenzenes, phenylene oxide sorbents, carbonaceous resins, polyurethane foam, alumina, silica gel, molecular sieves, C<sub>18</sub> reverse phase sorbents, cyano reverse phase sorbents, and activated carbon. Twelve sorbents from this group are recommended for initial screening studies to determine their effectiveness at sorbing low levels of explosives in water.

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## I. INTRODUCTION

### A. Background

Traditionally, trace organic pollutants present in water are analyzed by liquid-liquid extraction from water and concentration of the extract before instrumental analysis. This process necessitates the transportation of heavy, bulky containers of water to a laboratory, since, typically, one to ten liters of water are required for a single analysis. This process is both time consuming and labor intensive.

An attractive alternative to this process would be an "in field" concentration of the organics found in water onto a solid sorbent. The sorbent could be contained in an inert cartridge and a metered amount of water could be pumped through the cartridge. The advantages of this process include convenience, the ability to quantitate ppb levels of organics, and the recovery of polar organics such as phenol, which are not extracted quantitatively from neutral solutions with solvent-solvent extraction techniques.

A good sorbent for this type of sampling must adsorb essentially 100% of the organics of interest. The recovery from the sorbent must also be essentially 100%. The sorbates should not participate in "in situ" reactions on the sorbent. The sorbates should be easily desorbed with a minimum of solvent. Thermal desorption should be investigated, because the sorbates could be desorbed directly onto a GC for analysis.

### B. Objectives

The objective of this study was to survey and evaluate the available information pertaining to the use of solid sorbents for the concentration of selected explosives from water. The collected literature was evaluated with the ultimate goal of identifying sorbent technology capable of improving the analytical detection limits for the explosives of interest into the low parts per billion range. As a result of this literature evaluation, twelve sorbents which have potential for water sampling of explosives were selected for laboratory evaluation.

The explosives of interest in the study include 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), 2,6-dinitrotoluene (DNT), 1,3,5-trinitro-1,3,5-triazine (RDX), pentaerythrite tetranitrate (PETN), nitroglycerine, lead styphnate, tetracene, picric acid and tetryl.

### C. Study Methodology

The information evaluated in this study was gathered through computerized and manual literature searches and personal communications with manufacturers of various sorbent materials. The computerized data bases searched included Chemical Abstracts, National Technical Information Service (NTIS), Enviroline, Pollution Abstracts, Air Pollution (APTIC), Dissertation Abstracts, and Government Printing Office (GPO). The following criteria were used for

evaluation of the various sorbents and for selection of the sorbents to be included in the laboratory study.

- the efficiency of adsorption of organics, especially nitroorganics, from water
- potential interferences in the adsorption process
- the efficiency of solvent or thermal extraction of organics, especially nitroorganics from the sorbent
- potential for "in situ" reactions of the sorbate on the sorbent
- capacity of the sorbent for nitroorganics

This report presents an evaluation of the available data on sorbents for removal of explosives from water. The theory of the sorption process is briefly discussed, and the properties of various sorbents and results of previous environmental studies using these materials are presented. The selection of sorbents to be evaluated in the laboratory and the reasons for their choice are included at the end of the report.



## II. BASIS OF SORBENT PROCESSES

Sorbent materials can be classified into three basic types based upon the particular sorption process involved. The sorption process can involve:

- the trapping of sorbate molecules in micro-pores of appropriate size
- a direct sorbent-sorbate interaction of a hydrophilic or hydrophobic nature
- actual solution of the sorbate in a psuedo "liquid" sorbent
- a combination of these characteristics.

In general, sorbents typically exhibit adsorption by two or more of these processes.

Molecular sieves and activated carbon are examples of trapping in micropores. Both molecular sieves and activated carbon have a structure consisting of macropores and micropores, the latter being on the order of molecular dimensions. The application of the material is dictated by the relative size of the pores to the size of the solute and solvent molecules. Molecular sieves have pore sizes generally less than 10Å and are thus best suited for trapping small molecules such as water or low molecular weight alcohols from organic solvents. Activated carbon, on the other hand, has pore sizes in the 10-1000 Å range and can trap a wide variety of solutes.

The second process involving adsorption via direct sorbent-sorbate interaction of either a hydrophilic dipole-dipole nature or a hydrophobic Van der Waals type of interaction can be illustrated by silica and carbon sorbents. The surface of silica is composed of polar silicon-oxygen or silicon-hydroxyl functional groups which exhibit a strong dipolar attraction with any polar solute, and are thus best suited to the removal of polar materials from a non-polar solvent. Carbon and the various polymeric organic sorbents are basically non-polar materials. Non-polar solutes are attracted to these materials by a non-ionic Van der Waals interaction much in the same way that the hydrophobic end of a detergent molecule is attracted to a non-polar oil molecule.

The third process occurs with non-crystalline sorbents. These types of sorbents include semi-liquid organic polymers and bonded or non-bonded liquid phases on a crystalline support base. This process is essentially a partition of solute solubilities between the solvent (water) and the semi-liquid sorbent. It is most effective when the solute is much more soluble in the sorbent than in water. Thus, liquid sorbents cannot be used to remove polar, water soluble organics from water.

For sorption of organics from water, the sorbent should have a relatively large pore size, preferably in the 10-100 Å range. The surface properties of the sorbent should be of a hydrophobic nature. Finally, the sorbent should have solubility properties as similar to the solute as possible.

*why say this and then recommend Chromasorb 104 which has a pore size of 600-800 Å*



### III. MACRORETICULAR RESINS

Macroreticular resins are synthetic polymers with high porosity and large surface areas. Typical pore diameters range from 50 to 800 Å and typical surface areas range from 140-800 m<sup>2</sup>/g. The resins are generally chemically stable up to 200°C, although some resins can tolerate higher temperatures.

The most common macroreticular resins are polymers of styrene divinyl benzene, acrylic esters, or phenylene oxide. The polymers can have functional groups incorporated chemically into their structures. Common functional groups incorporated in the polymers are acrylonitrile, vinyl pyridine, vinyl pyrrolidone and ethylene glycol dimethacrylate (Analabs, 1980). These functional groups provide chemical selectivity to the polymer which, when combined with size and shape selectivity, yields excellent chromatographic separation of materials.

#### A. Styrene Divinylbenzene Resins

Styrene divinylbenzene resins are composed of very small gellular microspheres fused into large macrospheres. The space between the agglomerated microspheres is continuously porous. These resins are nonpolar and exhibit high sorbent capacity for nonpolar sorbates (Pietrzyk and Chu, 1977). The structure of a typical styrene divinylbenzene resin, one of the Amberlite XAD series, is shown in Figure 1. Physical properties and typical applications of several commercially available styrene divinylbenzene resins are listed in Table I. Common styrene divinylbenzene resins are Chromosorb 101 and 102, Porapak P, and Amberlite XAD-2 and XAD-4.

The Amberlite XAD resins require preconditioning before they can be used for environmental sampling. For air sampling, Van Rossum and Webb (1978) suggest sequential solvent extraction with acetone, methanol and methylene chloride or chloroform. The treated resins should be stored under a solvent such as methanol until needed to prevent sorption of organics while in storage. For water sampling, Rohm and Haas (1978) suggest preconditioning of XAD columns by backwashing with distilled water for approximately ten minutes, followed by downflow of four bed volumes of methanol to remove any traces of preservatives or monomeric components, followed by four bed volumes of distilled water. Since untreated XAD-2 and XAD-4 resins will not be wetted by water, dry sorbent should be wetted with methanol or ethanol before reconditioning.

The styrene divinylbenzene polymers have been used for both air and water sampling of organic pollutants. Of these resins, the Amberlite XAD series resins have been extensively studied for their ability to retain organic pollutants from air and water samples. Available data on air and water sampling with styrene divinylbenzene resins are summarized in Table II.

In air, humidity appears to have some effect on the capacity for organics of XAD-2. Expressed as V<sub>g</sub> (ml of sorbate per gram sorbent), Table III shows that sorbent capacity is decreased by as much as 17% at high relative humidity, although the decrease is much smaller for non-polar organics. Sydor and



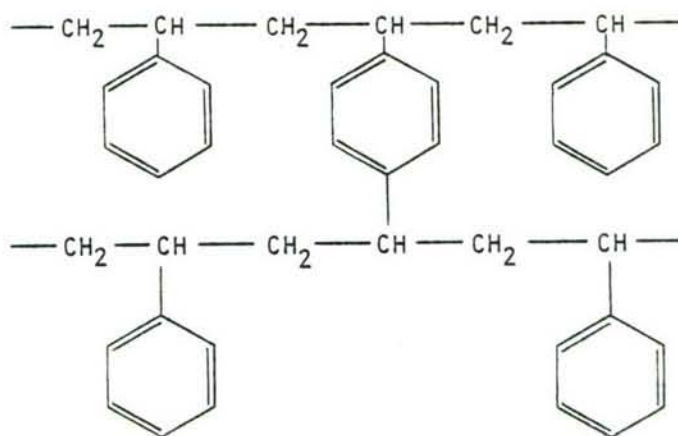


Figure 1. Structure of Amberlite XAD-2 and XAD-4 Resins (Kunin, 1976)

TABLE I. Properties of Styrene Divinylbenzene Resins

Porous Polymer	Polarity	Surface Area (m <sup>2</sup> /g)	Avg. Pore Diameter (Å)	Water Affinity	Temp. Limit °C	Application	Reference
Chromosorb 101	Non-polar	< 50	3000-4000	hydrophobic	275°(325°)*	Fast efficient separation of free fatty acids, glycols, alcohols, alkanes, esters, ketones, aldehydes, hydrocarbons, ethers, etc.	Johns Manville (1980)
Chromosorb 102	Slightly Polar	300-400	85	hydrophobic	250°(300°)*	Alcohols, light and permanent gases, oxygenated compounds, adsorbent to trap organics from air or water, etc.	Johns Manville (1980)
Porapak P	Non-polar	110	150	-	250°	Separates a wide variety of carbonyl compounds, glycols and alcohols.	Snyder et al. (1976) Analabs (1980)
Ambersorb XAD-2	Non-polar	300	90	hydrophobic	200°-250°	Concentration of water soluble steroids, surfactants, detergents, aromatic materials, adsorbent to trap organics from air or water.	Snyder et al. (1976) Rohm and Haas (1978)
Ambersorb XAD-4	Non-polar	784	50	hydrophobic	200°-250°	Concentration of organics, aromatics, adsorbent to trap organics from air or water.	Kunin (1976) Snyder et al. (1976)
Porapak Q(a)	Non-polar	840	75	-	250°	Particularly effective for hydrocarbons, organic compounds in water, and oxides of nitrogen.	Snyder et al. (1976) Analabs (1980)

\*Maximum temperature for short duration (a)ethyl vinyl benzene-divinyl benzene

TABLE II. Summary of Sorbent Data Available on Styrene Divinylbenzene Resins

Sorbent	Media	Chemicals Sorbed	Capacity	I solution	Recovery	Comments	Reference
Porapak P and Q Chromosorb 101 & 102	air	acetonitrile, t-butanol methyl ethyl ketone, benzene	mg sorbate/g sorbent NG	NG	NG	Porapak Q had highest overall sampling capacity	Butler & Burke (1976)
Amberlite XAD-2	air	assorted organics	NG	0.023-4.8	NG		Sydor & Pietrzyk (1978)
Amberlite XAD-4			NG	0.40-8.7	NG		
Porapak P			NG	.04-1.4	NG		
Porapak Q			NG	.18-3.5	NG		
Chromosorb 101 Porapak Q	air	assorted organics	NG	NG	NG	>90% efficient for trapping vapors	Pellizzari et al. (1975a)
Amberlite XAD-2	ethanol- water	assorted nitro- and chlorophenols	NG	NG	>95%	XAD-2 was used as column chromatography support	Grieser and Pietrzyk (1973)
Amberlite XAD-2	air	n-butyl amine, assorted organics	.238 mg/g .107-.357 mg/g	NG NG	NG NG	some irreversible adsorption occurs for higher boiling adsorbates	Gallant et al. (1978)
Amberlite XAD-2	air	phenol phenol-formaldehyde	NG	NG	93-98%	recovery for phenol in pre- sence of formaldehyde is slightly lower than recovery for phenol alone	Levin and Nilsson (1977)
Amberlite XAD-2 Amberlite XAD-4	water	assorted organics	NG NG	NG NG	NG NG	Higher adsorption and re- coveries were found for SDVB resins than for activated carbon, acrylic esters, carbonaceous resins and anion exchange resins	Glatz et al. (1979)
Amberlite XAD-2 Amberlite XAD-4	water	assorted organics	NG NG	NG NG	44-93% 69-83%	Phenol recovery only, 14% Phenol recovery only, 38%	Van Rossum and Webb (1978)
Amberlite XAD-2 Amberlite XAD-4 Duolite L-863	water	assorted organics	NG NG NG	NG NG NG	NG NG NG	L-863 gives 1.6 times better recoveries than Amberlite XAD-2. Amberlite XAD-4 gives 2.6 times better recoveries than XAD-2.	Chriswell et al. (1977)
Amberlite XAD-4	water	TNT and RDX	0.435 g TNT/g sorbent 0.05 g RDX/g sorbent	NG NG	NG NG	Amberlite regenerated but recovery data not given	Stevens et al. (1975)
Amberlite XAD-4	water	TNT, HMX, RDX, tetryl	0.24-0.28 g TNT/g sorbent 0.057 g RDX/g sorbent 0.009 g HMX/g sorbent 0.005 g tetryl/g sorbent	NG	NG	TNT will displace HMX, RDX, or tetryl	Szachra (1978)
Amberlite XAD-2	water	assorted organics pesticides	NG NG	NG NG	17-97% 24-96%	Although some compounds show low recoveries, most com- pounds showed recoveries of 80% or better	Harris et al. (1980)

NG - Not given

TABLE III. Comparison of  $V_g$ 's for Sorbates at Two Different Relative Humidities on XAD-2 (Pieciewicz et al., 1979)

Sorbate	Column Temperature (°C)	% Moisture (vol/vol)	% Relative Humidity	$V_g$ (ml/g)	Relative $V_g$ wet/dry
Pentane	53.1	0	0	1080	-
	53.2	10.9	87	1090	1.00
2-Butanone	53.1	0	0	3430	-
	53.5	9.8	76	2480	0.83
Ethanol	53.1	0	0	280	-
	54.0	10.8	82	244	0.87
Ethyl Bromide	55.0	0	0	640	-
	54.1	11.0	83	615	0.96



Pietrzyk (1978) report that Amberlite XAD-2 and XAD-4 show a decrease in capacity of 24% and 12% respectively in humid atmosphere.

A number of investigators have studied the recovery of organics from water by styrene divinylbenzene resins, and the results of several of these studies are summarized here.

Van Rossum and Webb (1978) used the XAD resins to isolate organic pollutants from water. Styrene divinylbenzene resins included were XAD-2 and XAD-4. The resins were used alone and in mixed beds. Recoveries for the various organic species tested using distilled water and tapwater are presented in Tables IV and V, respectively. The reduced recoveries from tapwater are attributed to reaction of the organic compounds with residual chlorine and other materials in the tapwater. Pellizzari and Bunch (1979) also reported that "in situ" reactions occur on XAD-2 in the presence of olefins and chlorine.

Chriswell et al. (1977) studied the recovery of organic materials sorbed from water using several types of sorbents, including Amberlite XAD-2, XAD-4, XAD-7 and XAD-8, several weak base anion exchange resins, and activated carbon. Recoveries were determined relative to the recovery of the XAD-2 resin. Duolite L-863 a styrene divinylbenzene resin manufactured by Diamond Shramrock was 1.6 times more effective than Amberlite XAD-2. Amberlite XAD-4 was 2.6 times as effective as XAD-2. Amberlite XAD-7 and XAD-8 were both 0.6 times as effective as XAD-2. All the other materials tested showed less than 0.2 times the recovery of Amberlite XAD-2.

Harris et al. (1980) also evaluated solid sorbents for water sampling. Among the sorbents considered were Amberlite XAD-2 and XAD-4. Amberlite XAD-2 was used to remove chlorinated pesticides from waste water with recoveries of greater than 89% of the pesticides. The pesticides were desorbed from the resin by elution with diethyl ether. Amberlite XAD-2 was also used to remove polyaromatic hydrocarbons from water with recoveries of 45 to 76%. The XAD-2 resin also removed trihalomethanes from water with greater than 60% recovery. Amberlite XAD-4 was used to remove trihalomethanes and chlorinated pesticides/PCB with recoveries of greater than 85% and greater than 70%, respectively.

Amberlite XAD-2 or 4 show the greatest affinity for non-polar organics, however, Gallant et al. (1978) have found XAD-2 effective for sorbing alcohols, phenols, alkyl amines and carboxylic acids in addition to less polar organics. Grieser and Pietrzyk (1973) found nitro phenol and picric acid retained by XAD-2 to a lesser extent than less polar organics.

Stevens et al. (1975) used Amberlite XAD-4 to remove TNT and RDX from munition waste water. These investigators found the capacity of Amberlite XAD-4 for TNT to be 0.435 g TNT/g XAD-4. The capacity of XAD-4 for RDX was 0.05 g RDX/g XAD-4. These capacities of XAD-4 were approximately twice the capacity of activated carbon (Filtersorb 300). Approximately 600 bed volumes of "red" water (TNT concentration approximately 100 mg/l) were run through the XAD-4 resin bed before breakthrough occurred. Flow rate was 1 gpm/ft<sup>3</sup>. The spent Amberlite XAD-4 could be regenerated with two bed volumes of acetone.

TABLE IV. Percent Recovery of Organics from Distilled Water by Amberlite XAD Resins  
(Van Rossum and Webb, 1978)

Compound	XAD Resins and Mixtures***									
	2/4	8	2/7	2	2/8	2 1/4	7	8 1/4	4 1/8	CH <sub>2</sub> Cl <sub>2</sub> *
Acenaphthene	72	68	20	81	99	85	84	81	81	91
2-Benzethiazole	40	80	53	75	74	73	77	82	82	96
bis(2-Chloroisopropyl)ether	-**	74	77	76	76	77	71	80	77	92
p-Cresol	33	58	47	50	44	49	60	69	68	50
Dibenzofuran	73	70	95	83	93	86	85	82	84	92
n-Hexadecane	3	-	-	8	3	18	14	-	11	36
1-Methylnaphthalene	64	62	80	75	76	82	80	77	79	86
2-Methylnaphthalene	63	61	77	72	75	80	81	77	77	86
o-Nitrotoluene	53	75	77	79	82	81	81	83	83	91
Naphthalene	64	66	78	77	79	81	82	80	80	87
Phenol	19	30	29	32	14	33	41	38	46	19
α-Terpineol	36	76	62	77	81	75	75	80	80	92
sym-Tetrachloroethane	35	58	59	66	61	68	68	72	72	82
Averages excluding n-Hexadecane	51	65	69	70	71	72	74	75	76	80

\* Sample transferred from a beaker to a separatory funnel to simulate adsorption on reservoir wall and then directly extracted with two 50 ml portions.

\*\* Peak unsuitable for accurate quantitation.

\*\*\* Mixtures are of equal dry weights of each resin.



TABLE V. Percent Recovery of Organics from Tapwater by Amberlite XAD Resins  
(Van Rossum and Webb, 1978)

Compound	Retained on Reservoir Wall		Recovered from Resin		In Aqueous Effluent from Column	
	XAD-2	XAD-48	XAD-2	XAD-48	XAD-2	XAD-48
Acenaphthene	0	2	79	80	0	0
Acenaphthylene	0	0	38 (84)*	42 (83)	0	0
2-Benzothiazole	0	0	69	77	26	30
Camphor	0	0	83	87	5	2
bis(2-chloroethyl)ether	0	0	41 (110)	79 (94)	47	11
bis(2-chloroisopropyl)ether	0	0	85	90	8	0
Di-n-butyl phthalate	4	4	91	92	0	-
Di-(2-ethylhexyl)phthalate	22	19	19	26	43	-
p-Dichlorobenzene	6	6	71	75	0	0
Dimethyl phthalate	0	0	116	113	0	-
Fluoranthene	0	0	85	85	0	-
Hexachlorobenzene	15	11	39	47	28	-
Hexachlorobutadiene	27	30	47	49	0	0
Hexachloroethane	11	12	66	69	0	0
n-Hexadecane	10	19	16	28	42	31
Naphthalene	10	0	84	86	0	0
o-Nitrotoluene	0	0	80	87	0	0
Phenol	0	0	0 (34)	9 (70)	6	0
Pyrene	5	0	64	68	11	-
α-Terpineol	0	0	5 (82)	5 (88)	0	0
1,1,3,3-Tetrachloroacetone	0	0	0 (22)	0 (53)	0	0
Tri-n-butylphosphate	4	12	85	72	0	0
2,4,6-Trichlorophenol	0	0	20	25	0	0
n-Tridecane	37	43	4 (5)	9 (6)	18	15

\* Values in parentheses are for distilled water.

Szachta (1978) summarized the studies on the removal of TNT and RDX as well as HMX and tetryl from waste water. Amberlite XAD-4 could remove TNT, HMX, RDX and tetryl from munition waste streams to the level of less than 1 ppm total nitrobodyes. Amberlite XAD-4 has a greater affinity for TNT than for the other nitrobodyes. At high concentrations of nitrobodyes, competition for sorption sites on XAD-4 occurs, and earlier breakthrough of nitrobodyes is found. TNT is adsorbed more rapidly than the other nitrobodyes.

While there has been some work done on desorption of organics, none has related directly to the recovery of explosives. Levin *et al.* (1977) investigated the recovery of phenol from XAD-2. It was found that 97 to 98% of the sorbed phenol could be removed by shaking the resin with diethyl ether. If a phenol-formaldehyde mixture was sorbed by XAD-2, the recovery dropped to 93-95%. Harris *et al.* (1980) found that polyaromatic hydrocarbons could be removed from Amberlite XAD-2 with methylene chloride and that diethyl ether could be used to remove pesticides and trichloromethanes from XAD-2 and from XAD-4. Grieser and Pietrzyk (1973) report that nitrophenol and picric acid are released from XAD-2 when the pH of the eluting solvent is increased.

#### B. Acrylic Esters

The common acrylic ester resins are Amberlite XAD-7, Amberlite XAD-8, Chromosorb 107, Chromosorb 108, and Porapak T. The structures for Amberlite XAD-7 and XAD-8 are given in Figure 2. The structures for the other resins are similar. Because of the polarity of the acrylic esters, these resins exhibit a greater affinity for polar sorbates than the styrene divinylbenzene resins (Pietrzyk and Chu, 1977). In addition, the sorbent Porapak T exhibits some water retention (Analabs, 1980). The physical characteristics of these resins are given in Table VI.

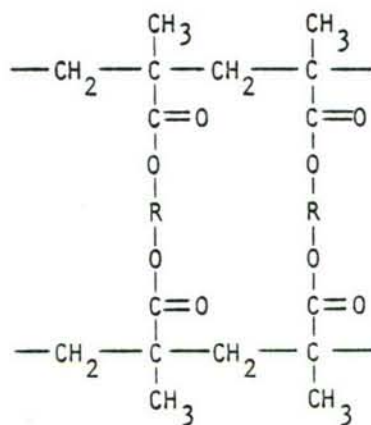
The acrylic resins have not been studied to the same extent as the styrene divinylbenzene resins. Chriswell *et al.* (1977) found that both XAD-7 and XAD-8 showed recoveries of organic contaminants from water of 0.6 times the recoveries found with Amberlite XAD-2. The acrylic esters were more efficient than either anion exchange resins or activated carbons. Sydor and Pietrzyk (1978) found that Amberlite XAD-7 had a higher sorbent capacity than XAD-2 for removal of low molecular weight compounds from an air stream. Sorption data on acrylic esters are summarized in Table VII.

#### C. Phenylene Oxide Resins

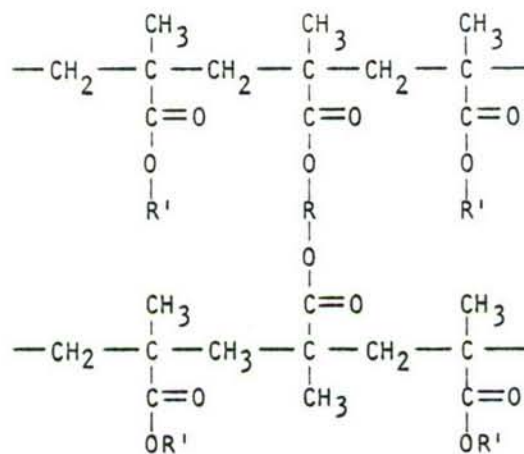
Tenax GC is a porous polymer of 2,6-diphenyl-p-phenylene oxide. Its structure is shown in Figure 3. It was developed as a GC packing material and exhibits the following features (Applied Science Division, undated).

- 1) high maximum operating temperatures (375°C)
- 2) short retention times
- 3) stable baseline after short conditioning time





Amberlite XAD-7



Amberlite XAD-8

Figure 2. Structures of Amberlite XAD-7 and XAD-8 Resins (Kunin, 1976)

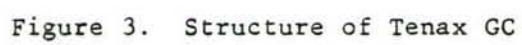
TABLE VI. Properties of Acrylic Ester Resins

Porous Polymer	Polarity	Surface Area m <sup>2</sup> /g	Avg. Pore A	Water Affinity	Temperature Limit (°C)	Application	Reference
Amberlite XAD-7	Intermediate polarity	450	90	-	200-250	Removal of organics from water	Snyder et al., (1976) ——— Kunin (1976)
Amberlite XAD-7	Intermediate polarity	140	235	-	200-250	Removal of organics from water	Snyder et al., (1976) ——— Kunin, (1976)
Chromosorb 107	polar	400-500	80	hydrophilic	225-250	Formaldehyde, sulfur gases, efficient for moderately polar compounds. Adsorbent to trap vinyl acetate from air.	Johns Manville (1980)
Chromosorb 108	polar	100-200	25	hydrophobic	225-250	Gases, alcohols, aldehydes, ketones, glycols, etc. Retention character- istics differ from other Century Series supports.	Johns Manville (1980)
Porapak T	polar	450	91	hydrophilic	190	Highest polarity and greatest water retention. Determination of for- maldehyde in aqueous solutions.	Waters Associates (1977) Analabs (1980)

TABLE VII. Summary of Sorbent Data Available on Acrylic Esters

Porous Polymer	Media	Chemicals	Sorbent capacity g sorbate/g sorbent	% Sorption	% Recovery	Comments	References
Porapak T	air	acetonitrile, benzene, t-BuOH, methyl ethyl ketone	NG	NG	NG	Porapak T shows higher sampling capacity for acetonitrile than styrene divinyl benzene resins	Butler and Burke (1976)
Amberlite XAD-7	air	assorted organics	NG	0.75-7.6	NG	Highest uptake shown for dimethyl formamide	Sydor and Pietrzyk (1978)
Amberlite XAD-7 Amberlite XAD-8	water	assorted organics	NG NG	NG NG	33-72% 47-95%	Phenol had a recovery of only 19% Phenol had a recovery of only 29% while acenaphthene recovery was only 20%	VanRossum and Webb (1978)
Amberlite XAD-7 Amberlite XAD-8	water	assorted organics	NG NG	NG NG	NG NG	Recovery was 61% of the XAD-2 recovery Recovery was 65% of the XAD-2 recovery	Chrissell et al., (1977)





4) effective separation at relatively low temperatures

Tenax GC is a low capacity sorbent (Sydor and Pietrzyk, 1978). The surface area of the polymer is  $19 \text{ m}^2/\text{g}$  (Butler and Burke, 1976), and the sorbent contains pores varying from  $30 \text{ \AA}$  to  $10,000 \text{ \AA}$  (Sakodynskii *et al.*, 1974). The retention volume/unit weight of adsorbent ( $V_g$ ) is much lower for Tenax than for other sorbents (Butler and Burke, 1976). Table VIII gives the relative column capacities ( $V_g \times$  relative packing density) of Tenax GC, Porapak P, T, R and Q and Chromosorb 101 and 102 for some volatile organics. As can be seen, Tenax consistently has the lowest capacity for these volatile organics (Butler and Burke, 1976). This is also shown graphically for acetonitrile in Figure 4. A summary of sorbent data available for Tenax GC is given in Table IX.

There are conflicting claims concerning Tenax GC's sorbent ability in the presence of water. According to Battelle, Columbus Laboratories (1979), humidity affects the recovery of organics from Tenax. Brown and Purnell (1979) claim that breakthrough on Tenax GC is affected by vapor concentration, but that humidity appears to have no affect on retention volumes. Kuo *et al.* (1977) used Tenax GC as a sorbent for water soluble organics which were gas-purged from water. When the purging gas contained high water vapor concentrations, displacement of organics from the polymer and more rapid breakthrough were observed. Novotny *et al.* (1974) found that water vapor was not retained by Tenax GC but condensation of water on the sorbent decreased the sorbent ability of Tenax GC. Barrett (1976) claims 100% recovery with nitroglycerin or ethylene glycol dinitrate independent of humidity. Pieciewicz *et al.* (1979) showed that a variation of humidity from 0% to 80% would result in a decrease in retention volume on Tenax GC. The decrease varied from 22 to 43% depending upon the nature of the volatile organic. Table X presents the comparison of retention volumes at 0 and 80% relative humidity using Tenax GC sorbent. Pellizzari *et al.* (1976) claim that sorbent ability is not affected by humidity levels up to 50%.

There is evidence of Tenax GC decomposition to diphenyl quinone (DPQ) in the presence of nitrous oxide (Battelle, Columbus Laboratories, 1979). The mixture of sulfur dioxide, nitrous oxide and water also react with Tenax GC to give DPQ (Neher and Jones, 1977; Vick *et al.*, 1977). Bunch *et al.* (1980) report "in situ" reaction on Tenax GC to form nitrosamines in the presence of  $\text{NO}_x$  and ozone. Nitrosamines could also be formed by reaction of secondary amines and nitrogen oxide on the Tenax GC surface. Morpholine has been shown to react with as little as 4 ppm  $\text{NO}_x$  to form 50% nitrosated morpholine (Rounbehler *et al.* 1980). Other "in situ" reactions include the formation of dichlorohexane and trichlorohexane in the presence of chlorine gas. Bromoform and dibromocyclohexane are formed on Tenax GC in the presence of bromine gas (Bunch *et al.*, 1979). Precautions must be taken that the organics recovered from Tenax GC are not artifacts of such "in situ" reactions.

Tenax GC has been shown to be useful for analysis of alcohols, diols, phenols, amines, aldehydes and ketones (Applied Science Division, undated). The resin shows a greater affinity for alkanes, alcohols and amines than for aldehydes, ketones and phenols (Pellizzari *et al.*, 1975a). Barrett (1976) showed that Tenax GC retained both nitroglycerine and ethylene glycol dinitrate with 100% recovery from the sorbent.

TABLE VIII. Relative Capacities of Sorbents in 1/16" OD columns (Butler and Burke, 1976)

acetonitrile	Tenax << P < 101 ~ 102 < Q ~ R < T
t-butanol	Tenax << 101 << P << T << 102 << R ~ T
methyl ethyl ketone	Tenax < P << 101 ~ 102 ~ T ~ R < O
benzene	Tenax < P ~ 101 ~ T < 102 ~ Q ~ R

The ordering system is based on the following differences (d) in

$$\log (V_g^{20} \times RPD): \quad \sim d < .10$$

$$< .10 \leq d \leq .25$$

$$<< d > .25$$

P, T, Q, R = Porapak P, T, Q, R, respectively.

101, 102 = Chromosorb 101, 102, respectively.



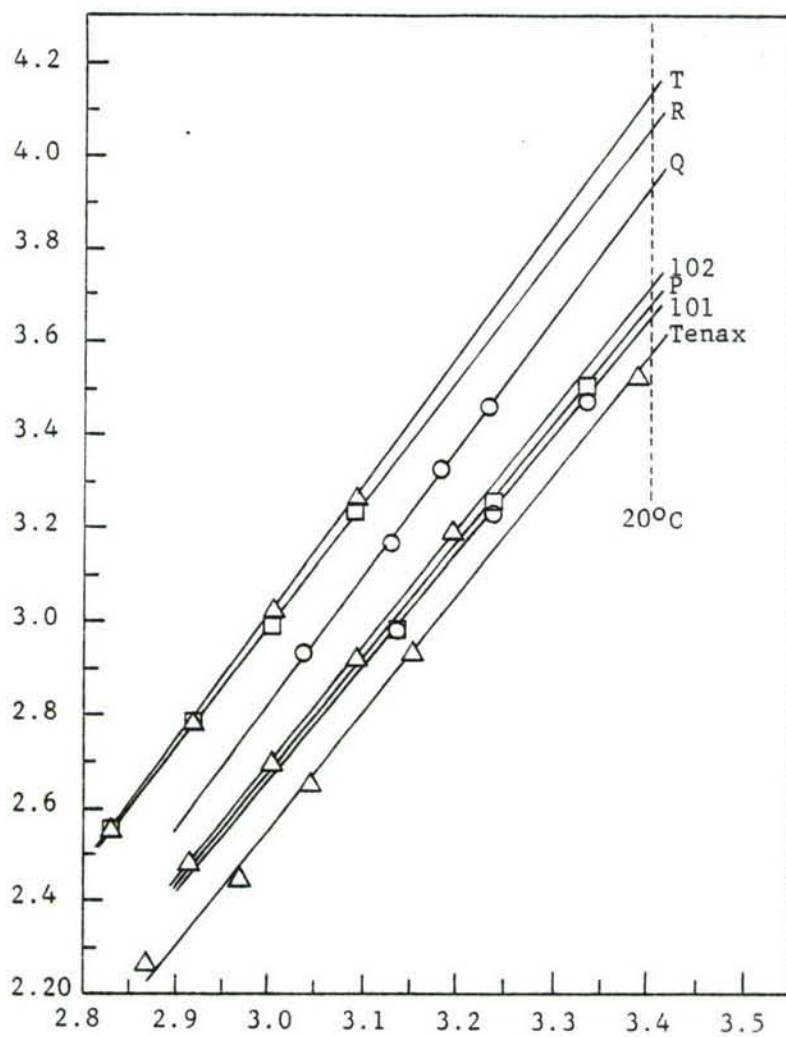


Figure 4. Plots of the Common Logarithm of Specific Retention Volume Versus Reciprocal Absolute Temperature Used to Determine  $\log V_g$  Values for Acetonitrile. (Butler and Burke, 1976).

TABLE IX. Summary of Adsorbent Data for Tenax GC

Sampling Media	Chemicals Tested	Sorbent Capacity mg sorbate/g sorbent	Z Sorption	Z Recovery	Comments	References
Air	alkanes	0.08-12.0	NG	NG	Tenax capacity was 50% or less than Amberlite XAD-2 capacity	Adams <u>et al.</u> , 1977
Air	acetonitrile, t-BuOH methyl ethyl ketone, benzene	NG	NG	NG	Tenax capacity lower than other porous resins	Butler and Burke, 1976
Air	assorted organics	NG	NG	NG	Adsorption efficiency >75% Desorption efficiency >80%	Kuo <u>et al.</u> , 1977
Air	polycyclic organics	NG	NG	30-106%	With Kuderna-Danish concentration of extracting solvents 90-95% recoveries were found	Neher, 1977
Air	assorted organics	NG	NG	58-95%		Pellizzari <u>et al.</u> , 1976
Air	assorted organics	NG	NG	60-100%	For 50 - 300 ng organics on 10.5 x 30 mm Tenax cartridge	Pellizzari <u>et al.</u> , 1975b
Air	assorted organics	NG	80-95%	NG	Sampling rate 0.25 L/min.	Pellizzari <u>et al.</u> , 1975a
Air	assorted organics					
Air	nitrosamines	NG	NG	NG	Tenax has low breakthrough volume for nitrosodimethylamine. Tenax prone to "in situ" formation of artifacts	Rounbehler <u>et al.</u> , 1980
Air	assorted organics	NG	0.09-1.62	NG	Uptake < 50% of uptake on XAD-2	Sydor and Pietryzk, 1978
Air	assorted organics	NG	>90%	>90%		Versino <u>et al.</u> , 1974
Air	nitroglycerin and ethylene glycol dinitrate		104%	100%	Concentration of ethylene glycol dinitrate ranged from 0.27-3.93 ug/m <sup>3</sup>	Barrett, 1976

TABLE X. Comparison of  $V_g$ 's for Sorbates at Two Different Relative Humidities on Tenax GC  
(Pieciewicz et al., 1979)

Sorbate	Column Temp. (°C)	% Relative Humidity	% H <sub>2</sub> O	$V_g$ (ml/g)	Relative $V_g^*$ $\frac{\text{wet}}{\text{dry}}$
Pentane	55.5	0	0	536.9	0.57
	54.4	0	0	532.4	
	54.8	83	11	313.7	
	54.4	78	10	295.5	
Ethyl bromide	55.5	0	0	704.0	0.78
	54.4	0	0	688.8	
	54.8	83	11	582.0	
	54.4	78	10	510.5	
2-Butanone	55.2	0	0	3234.9	0.69
	54.4	0	0	3134.2	
	54.8	83	11	2420.5	
	54.4	78	10	1976.9	
Ethanol	55.5	0	0	233.1	0.78
	54.4	0	0	268.3	
	54.8	83	11	205.6	
	54.4	78	10	186.3	

\*Relative  $V_g$ ,  $\frac{\text{wet}}{\text{dry}}$ , determined by taking the average wet  $V_g$  over the average dry  $V_g$  for a given sorbent.



Rounbehler et al. (1980) showed that when removing nitrosamines from air, Tenax GC showed an early breakdown. The Tenax GC air sampler showed 90% retention after 100 L of air had passed through the sampler. But at 190 L of air, retention had dropped to 7%.

Pellizzari et al. (1976) claim that Tenax GC air sampling cartridges showed good recoveries of sorbates after one week storage with a slight decrease in recovery of sorbates after 2 weeks. Tables XI and XII show the recoveries of various sorbates after storage. The recoveries shown in the data do not appear to be as good as those claimed by Pellizzari et al. (1976).

The high temperature stability of Tenax GC made the polymer a good candidate for solid sorbent hydrocarbon sampling tubes to be used for the collection and analysis of organics in air streams (Battelle, Columbus Laboratories, 1979). A sampling tube containing Tenax GC can be fitted to the inlet of a gas chromatograph (GC) and thermally heated. The organics sorbed on the Tenax would elute off the sorbent and be analyzed on line (Versino et al., 1974). This type of use would eliminate the need to recover organics sorbed on the polymer by solvent extraction. Thermal recovery of volatile organics from Tenax with immediate introduction to GC showed a recovery of 90-100% (Pellizzari et al., 1975b). None of the other common sorbents showed the temperature stability exhibited by Tenax GC.

The major advantage of Tenax GC is its high thermal stability. Sorbates can be removed from Tenax thermally and introduced directly into a GC. In addition, Tenax is particularly suitable for the sorption of high boiling compounds because the combination of high temperature limit and low retention volume would allow rapid desorption of high boiling compounds from Tenax GC.

#### D. Other Resins

There are several other solid sorbents resins commercially available. Some of the more popular resins are described in Table XIII. The functional groups on these resins make them more polar than the styrene divinylbenzene resins. These resins have so far received only limited study for use as sampling sorbents.

Butler and Burke (1976) compared Porapak R to Porapak P, Q and T, Tenax GC and Chromosorb 101 and 102 for the removal of model compounds from air (Table VIII). Porapak R, a vinyl pyrrolidone resin, exhibited high sampling capacities for the model compounds.

TABLE XI. Effects of Transportation and Storage on the Percent Recovery of Carcinogenic Vapors from Tenax GC<sup>a</sup> (Pellizzari et al., 1976)

Compound	Weeks Expired					
	Nontransported			Transported		
	0	1	0	1	2	
Glycidaldehyde	95	92 + 4	95	87 + 4	50 + 8	
$\beta$ -propiolactone	100	95 + 4	100	90 + 5	85 + 2	
Bis-(2-chloroethyl)ether	90	86 + 6	90	87 + 5	>95 + 2	
Ethyl methanesulfonate	100	85 + 5	100	83 + 6	>95 + 2	
Bitromethane	-	92 + 3	-	95 + 3	85 + 2	
Bis-(chloromethyl)ether	100	65 + 5	100	58 + 5	41 + 4	
Butadiene diepoxide	100	76 + 6	100	75 + 4	64 + 5	
N-nitrosodiethylamine	100	82 + 4	100	84 + 3	62 + 3	
Styrene oxide	100	71 + 5	100	68 + 6	70 + 7	

<sup>a</sup>Tenax GC cartridges were loaded with vapors (300 ng/component), shipped by air freight to San Francisco, California and immediately returned. Total transportation time was 6 days.

TABLE XII. Effect of Storage on the Percent Recovery of Vapors from Tenax GC Cartridges<sup>a</sup>  
(Pellizzari et al., 1976)

Compound	Weeks Expired		
	0	3	5
1-Nitropropane	95 + 2	93 + 3	50 + 9
Chlorobenzene	95 + 2	80 + 4	50 + 8
Phenyl methyl ether	95 + 2	95 + 2	70 + 8
N-Ethyl aniline	95 + 2	95 + 2	70 + 6
Nitrobenzene	95 + 2	95 + 3	50 + 9
Aniline	95 + 2	95 + 2	80 + 5
4'-Fluoroacetophenone	95 + 2	80 + 4	90 + 4

<sup>a</sup>Tenax GC cartridge samplers were loaded with vapors and immediately shipped air freight to Houston, Texas and returned in two weeks; 0.3 week period includes transport, 3-5 represents additional storage.



TABLE XIII. Physical Characteristics of Selected Macroreticular Resins

Porous Polymer	Type of Polymer	Polarity	Surface Area m <sup>2</sup> /g	Avg. Pore Diameter Å	Water Affinity	Max. Temp. °C	Application	Reference
Porapak R	Vinyl pyrrolidone	moderately polar	780	76	hydrophilic	250	Moderate polarity. Long retention and good resolution observed for ethers. Separation of esters. Separation of H <sub>2</sub> O from Cl <sub>2</sub> and HCl.	Analab, 1980 Snyder <i>et al.</i> , 1976
Porapak S	Vinyl pyridine	polar	670	76	-	250	Separation of normal and branched chain alcohols.	Analab, 1980 Snyder <i>et al.</i> , 1976
Porapak N	Vinyl pyrrolidone	polar	437	-	hydrophilic	190	Separation of CO <sub>2</sub> , NH <sub>3</sub> , H <sub>2</sub> O, and of acetylene from other C <sub>2</sub> hydrocarbons. High water retention.	Analab, 1980 Snyder <i>et al.</i> , 1976
Chromosorb 104	Acrylonitrile divinylbenzene	very polar	100-200	60-80	hydrophobic	250	Nitriles, nitroparaffins, H <sub>2</sub> S, xylenols, NH <sub>3</sub> , SO <sub>2</sub> , CO <sub>2</sub> , vinylidene chloride, vinylchloride, traces of water in solvents, etc.	Johns Manville, 1980
Chromosorb 105	polyaromatic	moderately polar	600-700	40-60	hydrophobic	250	Formaldehyde, acetylene from lower HC. Various classes of organic compounds in b.p. range 200°C, adsorbent to trap organics from air and water.	Johns Manville, 1980

#### IV. CARBONACEOUS RESINS

Rohm and Haas have developed a series of sorbents with chemical properties intermediate between activated carbon and polymeric resins. These sorbents, known as Ambersorb XE-340, XE-347 and XE-348, are experimental products not commercially available (Panza, 1981). The affinity for water exhibited by these sorbents varies from the hydrophobic XE-340 to the hydrophilic XE-348. Because of the unique structure found in these sorbents, the Ambersorb sorbents are characterized by superior performance to conventional adsorbents for many applications. The advantages of the Ambersorb sorbents include exceptional physical strength, attrition resistance and increased regeneration flexibility when compared to either activated carbon or to polymeric adsorbents (Rohm and Haas, 1977). The physical characteristics of these sorbents are summarized in Table XIV.

Ambersorb XE-340 was designed to sorb nonpolar organics from air or water. It has been proven effective for removing pesticides, such as dieldrin or DDT, halogenated hydrocarbons, and chlorinated ethers from water. Ambersorb XE-347 can be compared to a molecular sieve which separates mixtures by molecular size. The pore structure of Ambersorb XE-347 is an appropriate size and shape for separation of aromatic molecules and unsaturated hydrocarbons. The predominant application of XE-347 has been the removal of organics, such as vinyl chloride, toluene, ethyl arylate and cumene, from air streams. Ambersorb XE-347 is also suitable for sorption of organics such as ethanol and acetone from water. Ambersorb XE-348 is a wide spectrum sorbent capable of sorbing both polar and non-polar organics from either air or water. Ambersorb XE-348 behaves similarly to activated carbon. It can sorb a wide range of organics and, in addition, is easily regenerated either by solvent extraction or by steam extraction (Rohm and Haas, 1977).

Since these sorbents are still experimental products, not much literature is available on their usage. Harris *et al.* (1980) used Ambersorb XE-347 in conjunction with Amberlite XAD-2 for the removal of organics from water. A dual bed system was chosen because Ambersorb XE-347 has a greater affinity for polar compounds such as phenol than Amberlite resins. Recovery of phenol from water is particularly difficult. Phenol recovery utilizing Amberlite resins XAD-2, XAD-7 and XAD-8 is only 14%, 19% and 29%, respectively (Van Rossum and Webb, 1978). In a dual bed system utilizing Amberlite XAD-2/XAD-8, Van Rossum and Webb (1978) reported recoveries of 46%. Ambersorb XE-347 is capable of recovering 46.8% of the phenol.

TABLE XIV. Typical Physical Properties of Ambersorb<sup>TM</sup> Resins

	Ambersorb XE-340	Ambersorb XE-347	Ambersorb XE-348
Appearance	black, spherical non-dusting	black, spherical non-dusting	black, spherical non-dusting
Total Surface Area (N <sub>2</sub> , BET method), m <sup>2</sup> /gm	400	350	500
Bulk Density, lbs/cu.ft.	37	43	37
Bulk Density, g/cm <sup>3</sup>	0.60	0.70	0.60
Particle Density, g/cm <sup>3</sup> (Hg displacement)	0.92	1.05	0.91
Skeletal Density, g/cm <sup>3</sup> (He displacement)	1.34	1.85	1.95
Pore Volume, cm <sup>3</sup> /g	0.34	0.41	0.58
Particle Size (U.S. Sieve Series)	20-50	20-50	20-50
Crush Strength, Kg/Particle	>3.0	>3.0	1.0
Ash Content, %	<0.5	<0.5	<0.5
Pore Size Distribution <sup>(1)</sup> :			
Diameter Range, Å	Vol. %		
< 6	0	50	16
6- 40	18	0	21
40-100	13	0	9
100-300	69	50	51
> 300	0	0	3

<sup>(1)</sup> Determined by a method similar to Walker et al., Fuel 45, 233 (1963).  
IN: Rohm and Haas (1977).



## V. OTHER TYPES OF SORBENTS

### A. C<sub>18</sub> Reverse Phase Sorbent

Silicone (C<sub>18</sub> H<sub>37</sub> SiO<sub>3/2</sub>)<sub>n</sub> surface bonded to a silica gel solid support is a common high pressure packing known as reverse phase C-18 packing. This C-18 packing has been useful for the removal of volatile organics such as car exhaust vapors and chlorinated hydrocarbons from air. Although these organics are effectively sorbed, there are some indications that the organics desorbed from the C-18 were artifacts of the sorbent (Aue and Teli, 1971). In addition, very volatile organic components in air tend to elute from the C-18 cartridge used in sampling.

Waters Associates, Inc. offers a C-18 packed cartridge called a SEP-PAK. These cartridges are designed to perform fast simple cleanup and concentration of organic residues prior to analysis by liquid chromatography (Waters Associates, 1979a). The C<sub>18</sub> SEP-PAK has been used to concentrate PCBs present at 1 ppb in water, concentrate residues up to one thousand times with 95% recovery, and concentrate large volume samples collected in the field (Waters Associates, 1979b).

Riggin and Howard (1979) used SEP-PAK C-18 cartridges to concentrate benzidine, dichlorobenzidine and diphenylhydrazine present in waste water. The C-18 cartridges allowed for the rapid concentration of the residues. In addition, the recovery of diphenylhydrazine, which is unstable in water, was greatly improved.

Most recently, J.T. Baker Chemical Co. (1981) has come out with a line of disposable extraction columns similar to the Waters SEP-PAK. The Baker extraction columns are packed with one, three or six ml of C<sub>18</sub> packing, which makes them more versatile than the Waters SEP-PAK which come in only one size.

Cyano resins are similar to the C<sub>18</sub> surface-bonded resins except that the -CH<sub>3</sub> end group is replaced by -CN. This type of material has intermediate polarity and will sorb strong polar groups better than the C<sub>18</sub> sorbent. Cyano surface-bonded to silica is available in cartridges from Baker and from SEP-PAK.

### B. Alumina, Silica Gel and Molecular Sieves

Alumina, silica gel and molecular sieves have all been considered as sorbents for air or water sampling, however they all absorb water more readily than organic materials. In addition, silica gel and alumina are structurally weakened by contact with liquid droplets (Kovach, 1978). Recoveries of 2-aminoethanol sorbed on silica gel dropped from 100 to 62% when the sorbent tube was stored at ambient temperatures (20°C) for 28 days. A drop of 15% was observed in the first three days of storage (Wood and Nichols, 1978). Since these sorbents show such an affinity for water, their suitability as solvents for water sampling is questionable.



### C. Ion Exchange Resins

Ion exchange resins depend upon electrostatic interactions for the removal or concentration of materials from water. These interactions could severely alter the sorbed material. For example, Hoffsommer *et al.* (1977) found that HMX, RDX and other nitrocompounds removed from water with the strongly basic anion exchange resins of the Amberlite IRA-400 series reacted on the resin to form nitrous oxide, ammonia, formaldehyde and nitrite ions. In addition, salts found naturally in ground water could cause premature elution of sorbed material. Harris *et al.* (1980) found that the anion exchange resins Amberlite IRA-93 and IRA-904 showed almost instantaneous breakthrough of sorbed polar organics when the eluting water contained as little as 250 ppm sodium chloride. This level of salt is not unusual for aqueous effluents, so if ion exchange resins are to be used for sorbing organics from natural aquifers, the salinity of the aquifer must be considered. Table XV summarizes sorbent data available on the use of ion exchange resins for removal of organics from water.

### D. Polyurethane Foam

Navratil *et al.* (1977) used open pore polyurethane (OPP) columns to remove polynuclear aromatic hydrocarbons from water. OPP is composed of an agglomeration of microspherical particles in a rigid permeable structure. The OPP columns are prepared "in situ" by the polymerization of toluene-carbon tetrachloride solutions of isocyanate and polyol. The structures of these materials are given in Table XVI. The polycyclic aromatic hydrocarbons studied are given in Table XVII. Recoveries of the polycyclic aromatic hydrocarbons varied from 56 to 100%. The polycyclic aromatic hydrocarbons were eluted from OPP using methanol. The recovery results are given in Table XVIII.

Polyurethane foam has also been considered for use as a sorbent for laboratory and river water. The extraction efficiencies of the foam were not as good as either solvent extraction of the water or extraction by XAD resins (Harris *et al.*, 1980).

### E. Carbon-Sulfur Compounds

Nonstoichiometric carbon-sulfur compounds ( $C_xS$ ) have been investigated for the sorption of phenol from water (Chang and Savage, 1981). Carbon-sulfur compounds behave similarly to activated carbon. The major difference lies with the carbon-sulfur surface of  $C_xS$  rather than the carbon-oxygen surface of the activated carbon. Since C-S is not as polar as C-O, it is postulated that aromatic groups would not bind to  $C_xS$  as tightly as they do to activated carbon.  $C_xS$  was found to have a larger capacity for phenol than Filtersorb 300. In addition, repeated regeneration with 2-propanol solvent extraction recovered 90% of the capacity of the  $C_xS$ .

### F. Activated Carbon

Activated carbon is an effective sorbent for the removal of most organic compounds from water. Activated carbon is composed of randomly oriented and

TABLE XV. Use of Ion Exchange Resins for Organic Sorption From Water

Ion Exchange Resin	Type	Materials Sorbed	Results	Reference
Duolite S-37	Weak base anion exchange	assorted organics	Recovery of 17% of the recovery found with Amberlite XAD-2	Chriswell <u>et al.</u> , 1977
Duolite A-7	Weak base anion exchange	assorted organics	Recovery of 15% of the recovery found with Amberlite XAD-2	Chriswell <u>et al.</u> , 1977
Duolite ES-561	Weak base anion exchange	assorted organics	Recovery of 7% of the recovery found with Amberlite XAD-2	Chriswell <u>et al.</u> , 1977
Amberlite A-26	Strong base anion exchange	various phenols	Average recovery of 97.7% of all phenols	Chriswell, <u>et al.</u> , 1975
Amberlite IRA-93	Weak base anion exchange	phenol	With NaCl content of 250 ppm, breakthrough was instantaneous	Harris <u>et al.</u> , 1980
Amberlite IRA-904	Strong base anion exchange	phenol	With NaCl content of 250 ppm, breakthrough was instantaneous	Harris <u>et al.</u> , 1980
Amberlite IRA-400	Strong base anion exchange	HNX, RDX explosives	Explosives degraded by ion exchange resin	Hoffsommer <u>et al.</u> , 1977
Dowex 1x2	anion exchange	humus materials	60-80% sorption	Sirotkina <u>et al.</u> , 1974
Dowex AV-17	anion exchange	humus materials	60-80% sorption	Sirotkina <u>et al.</u> , 1974
DEAE Cellulose	anion exchange	assorted organics	Sorption of naphthenic acid, tannin and phenol	Sirotkina <u>et al.</u> , 1974
CN Cellulose	cation exchange	assorted organics	No sorption	Sirotkina <u>et al.</u> , 1974

TABLE XVI. Materials and Reaction for Preparation of Open-Pore Polyurethane of Various Compositions (Navratil et al., 1977)

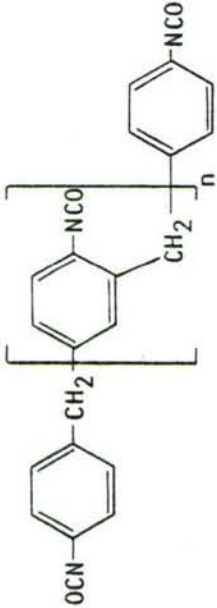


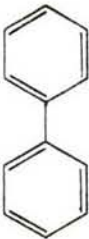
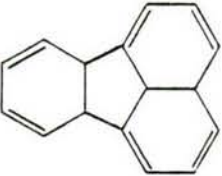


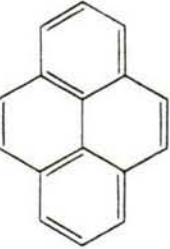
Trade Name	Structure	Grams of Material per 25 ml Solvent OH/NCO•IQ QH/NCO•2.2
Mondur MR (Mobay Chemical Co.)		3.16      2.00
LA-475 (Union Carbide Corp.)		2.84      4.00



TABLE XVII. Polycyclic Aromatic Hydrocarbons Studied (Navratil et al., 1977)

Compound	Structure
Benzo [a] pyrene (Aldrich, 98%)	
Biphenyl	
Fluoranthene (Aldrich, 98%)	
Naphthalene (Baker, reagent)	
Phenanthrene (Matheson, technical <sup>a</sup> )	
Pyrene (KBK, reagent <sup>a</sup> )	

<sup>a</sup>purified further by sublimation.



TABLE XVIII.. Recovery of Polycyclic Aromatic Hydrocarbons with Open-Pore Polyurethane  
(Navratil et al., 1977)

	Flow Rate, l/h	Loaded, µg	Recovery, %
Benzo[a]pyrene	1.8	4	95 + 6
Biphenyl	0.9-1.5	5-6	98 + 5
Fluoranthene	0.5-1.0	4-5	77 + 4
	0.5-1.0	1-2.5	97 + 3
Naphthalene <sup>a</sup>	0.1	5	56 + 3
	0.1-1.0	1-2.5	98 + 10
Phenanthrene	0.8-1.0	5	58 + 7
	0.8-1.0	1-2.5	92 + 9
Pyrene	0.6-0.8	1-4	100 + 2
	1.2-1.7	4-5	89 + 3
Pyrene (XAD-2) <sup>a</sup>	0.6	4	79 + 8

<sup>a</sup>Required 10 ml of methanol to elute quantitatively; others needed only 5 ml.

interfused graphite microcrystals. The interconnected crystals result in a porous, high surface area material. Carbon is activated by first heating to 170°C to remove water followed by heating to 275°C, prolonged heating at 400-600°C and finally by treatment with superheated steam at 750-950°C. The process burns off any hydrocarbon tar coating and enlarges the pore structure of the material. The resulting material has pore sizes varying from less than 20 Å to more than 500 Å. The sorption efficiency of the carbon is highly dependent on the shape, arrangement and size distribution of the pores (Jonas and Eskow, 1976; Cheremisinoff and Morresi, 1978).

The primary application of activated carbon has been the removal of organic pollutants from water in municipal drinking water or waste water systems. Efficiencies for removal of most organics are high. There are several examples of successful applications of activated carbon in the explosives industry (Cheremisinoff and Morresi, 1978). Szachta (1978) has investigated the relative capacities of activated carbon and XAD-4 in the treatment of "pink water" containing TNT, RDX, HMX and tetryl. Carbon proved to have a higher capacity for all nitrocompounds studied except TNT. - *higher capacity may not be the overriding factor*

Activated carbon has been used extensively to concentrate organics from water for analysis. The carbon adsorption method has several serious limitations, however. High quality activated carbon is not always available, necessitating lengthy preliminary cleanup steps to reduce background levels of organics. Many organics are adsorbed so strongly that desorption efficiencies are low and are not reproducible (Harris et al., 1980; Budde and Eichelberger, 1979).

Chriswell et al. (1977) determined the recovery of organic compounds for a series of sorbents. The recoveries were normalized to the recovery of Amberlite XAD-2. The results are given in Table IXX. The activated carbons gave recoveries from 0% to 40% of the recovery found on XAD-2. There are numerous references to the use of carbon adsorption for sampling, a few of which are listed in Table XX. There are also a number of methods which employ carbon sampling tubes (Taylor, 1977).

The difficulty of removing some organics from carbon has been attributed to chemisorption to reactive sites formed by the oxidative activation of the carbon (DeFilippi et al., 1980). It has also been pointed out that improved recoveries result if the carbon is dried well prior to extraction (Van Rossum and Webb, 1978). This suggests that the hydrophobic extraction solvent is being excluded from the pores by entrapped water. Improved results could be obtained by employing consecutive extractions first with a water soluble solvent such as acetone or ethanol before desorbing with a water insoluble solvent such as chloroform.

The variability of recoveries from different laboratories makes the choice of extraction solvent very difficult. For example, Chriswell et al. (1977) have suggested that diethylether is one of the best extraction solvents, while Huffman (1979) has listed the recoveries from ethylether as 0.6%, or almost 100 times less than chloroform. Carbon disulfide is one of the most

TABLE IXX. Recovery of Gas Chromatographable Organic Compounds (Chriswell et al., 1977)

Sorbent	Type	% Recovery of Gas Chromatographable Organic Compound Relative to XAD-2 Resin				
		Location				Average
		Ames	Ottumwa	Des Moines	Slater	
XAD-2	STDV	100	100	100	100	100
L-863	STDV	75	168	200	188	158
XAD-4	STDV	129	180	577	157	261
XAD-7	ACES	64	21	74	82	61
XAD-8	ACES	83	58	119	3	65
S-761	PHFA	28	10	44	-	21
S-37	AE	16	7	45	-	17
A-7	AE	26	2	32	-	15
ES-561	AE	-	-	26	-	7
Darco	Carbon	3	9	30	-	11
FS-300	Carbon	4	19	31	1	14
WVB	Carbon	17	14	40	-	18
WVG	Carbon	-	20	35	-	14
G-216	Carbon	1	8	26	3	10
G-107	Carbon	19	13	9	3	11
XE-340	Carbon Resin	35	37	24	9	26

STDV - Styrene divinyl benzene; ACES - Acrylic ester; PHFA - phenol formaldehyde; AE - Weak base anion exchange resin

TABLE XX. Activated Carbon Sampling Studies

<u>Compound(s) Studied</u>	<u>Matrix</u>	<u>Desorption Solvent(s)</u>	<u>% Recovery</u>	<u>Reference</u>
organics	water	freon ethyl ether methanol chloroform 0.1N HCl 0.1N NaOH steam	0.5 0.6 35 54 4 12 28	Huffman, 1979
Acenaphthene 2-Benzothiazole bis(2-chloroethyl)ether hexachlorobutadiene hexachloroethane n-hexadecane phenol tri-n-butylphosphate n-tridecane	water	chloroform	0 0 85 48 61 14 9 82 14	Van Rossum & Webb, 1978
organics	water	ethyl ether	0-40	Chriswell et al., 1977
methylethylketone toluene trichloroethylene butyl acetate 2-methylcyclohexane styrene	air	carbon disulfide	60-105 38-78 30-73 40-98 59-92 22-83	Graust and Hermann, 1966
PCBs (Aroclor 1260)	isopropanol	acetone methylene chloride benzene chlorobenzene	0 0 11-16 77-91	Unpublished results this laboratory, 1980



commonly employed desorption solvents (Taylor, 1977; Graust and Hermann, 1966), but comparisons of it to other organic solvents could not be located. Results obtained in this laboratory (1980) for PCBs demonstrated that chlorobenzene was superior to benzene, acetone or methylene chloride. Presumably the ideal desorption solvent should be as similar to the sorbate as possible.

A novel form of solvent extraction has been developed by DeFilippi et al. (1980). The solvent utilized is supercritical CO<sub>2</sub>. A large variety of organic compounds exhibit a dramatic increase in solubility near the critical liquid region. Supercritical CO<sub>2</sub> can regenerate carbon upon which organic pesticides had been sorbed. The resultant carbon has nearly 70% of the capacity of the virgin carbon. This implies that approximately 30% of the organics are not removed from the carbon. No data were available on recoveries from carbon. Another explanation for the loss in capacity on the carbon might be that interaction of water with active sites on the carbon which could inactivate the sites.

In addition to the problems encountered in removing organics from carbon, it is suspected that "in situ" chemical changes can occur on carbon. The types of organics desorbed may not represent the types of organics in the water being sampled (Harris et al., 1980).

Conti et al. (1978) mixed modified perlite with activated charcoal for purification of water. The role of the perlite was to increase the removal of non-polar organics from the influent. Modified perlite is a hydrophobic material coated with a layer of silicone oil. The perlite-charcoal mixture removed traces of organics from waste water. The resulting water was of drinking quality.

## VI. DISCUSSION AND CONCLUSIONS

A wide variety of sorbents have been identified which may have potential for sampling of organics from water. Although not all of these sorbents have been used in this application in the past, a number of them will be included in a laboratory screening program to determine their effectiveness in sorbing organics from water. Table XXI lists candidate sorbents and their manufacturers.

Most of the studies concerning the use of solid sorbents for water sampling examined styrene divinylbenzene resins such as Amberlite XAD-2 and XAD-4. Both these resins are potentially good sorbents for the nitro bodies of interest to ARRADCOM. Other styrene divinylbenzene resins are Chromosorb 102, which is chemically equivalent to XAD-2, Chromosorb 101 and Porapak P. Porapak has a larger pore size than Amberlite XAD-2 or 4 (150 Å), but its surface area is much lower (100 m<sup>2</sup>/g). Since sorbent capacity is related to surface area, Porapak P will not have the capacity of the XAD resins. Chromosorb 101 has a very low surface area (30-40 m<sup>2</sup>/g) with a very large pore size (3000-4000 Å) (Snyder et al., 1976). Since the mechanism for sorbent activity for styrene divinylbenzene resins has been postulated to involve van der Waal interactions and the surface area is so low, Chromosorb 101 will have very low capacity and may have only limited applicability to water sampling.

*again not necessarily the overriding factor!*

Amberlite XAD-7 and XAD-8, Chromosorb 107 and 108, and Porapak T are acrylate esters. The acrylate esters are expected to show higher capacity for polar sorbates than the styrene divinylbenzene resins (Pietrzyk and Chu, 1977). Chromosorb 104, an acrylonitrile divinylbenzene resin, has shown some success at sampling nitro compounds in air (Pellizzari et al., 1975a). Porapak Q, an ethylvinylbenzene divinylbenzene, has also been useful for sampling nitro compounds in air (Pellizzari et al., 1975a).

Tenax GC, a phenylene oxide sorbent, has received much attention for air sampling of organics. It is a low capacity resin (Butler and Burke, 1976) which could exhibit decreased capacity in aqueous media (Piecowicz et al., 1979). In addition, "in situ" reactions are known to occur on Tenax GC (Neher and Jones, 1977; Bunch et al., 1980; and Rounbehler et al., 1980). Tenax GC was not used for water sampling in any of the literature obtained for this search.

Carbonaceous resins appear very promising for water sampling. The Ambersorbs have sorbent abilities comparable to activated carbons, but the sorbates are more easily desorbed from the Ambersorb surface. Ambersorb XE-340, XE-347, and XE-348 differ widely in their sorbent properties and should each be compared with sorbents of similar polarity.

Activated carbon is an excellent sorbent which recovers a wide range of organic compounds from water. One of its major advantages is its low cost compared to other sorbents. Disadvantages are that desorption of sorbed materials from carbon is often difficult and that "in situ" reactions of sorbates are suspected.



TABLE XXI. Summary of Potential Sorbents

Sorbent	Type	Manufacturer	Specific Surface Area m <sup>2</sup> /g	Average Pore Size, Å
Amberlite XAD-2	Styrene Divinylbenzene	Rohm & Haas	330	90
Amberlite XAD-4	Styrene Divinylbenzene	Rohm & Haas	750	50
Amberlite XAD-7	Acrylic Ester	Rohm & Haas	450	80
Amberlite XAD-8	Acrylic Ester	Rohm & Haas	140	250
Ambersorb XE-340	Carbonaceous Resin	Rohm & Haas	400	100
Ambersorb XE-347	Carbonaceous Resin	Rohm & Haas	350	100
Ambersorb XE-348	Carbonaceous Resin	Rohm & Haas	500	100
Chromosorb 102	Styrene Divinylbenzene	Johns Manville	300-400	85
Chromosorb 103	Crosslinked Polystyrene	Johns Manville	15-25	3000-4000
Chromosorb 104	Acrylonitrile DVB	Johns Manville	100-200	600-800
Chromosorb 105	Polyaromatic	Johns Manville	600-700	400-600
Chromosorb 106	Crosslinked Polystyrene	Johns Manville	-	-
Chromosorb 107	Acrylic Ester	Johns Manville	-	-
Chromosorb 108	Acrylic Ester	Johns Manville	-	-
Porapak P	Styrene Divinylbenzene	Waters Assoc.	110	150
Porapak Q	Ethylvinylbenzene	Waters Assoc.	840	75
Porapak R	Vinyl pyrrolide	Waters Assoc.	780	76
Porapak S	Vinyl Pyridine	Waters Assoc.	670	76
Porapak N	Vinyl Pyrrolide	Waters Assoc.	437	-
Porapak T	Ethyleneglyco- dimethylacrylate	Waters Assoc.	450	91
Tenax GC	2,6-diphenyl p phenylene oxide (C <sub>18</sub> H <sub>37</sub> SiO <sub>3</sub> /2) <sub>n</sub>	Enka N.V.	19	720
Reverse Phase C-18 over Silica	-	Various	-	-
C-S Surface Carbon	-	Exxon Research	-	-
APC 12 x 46	Activated Carbon	Calgon	-	-
Filtrosorb 300	Activated Carbon	Calgon	-	-
Darco 5-51	Activated Carbon	Darco	-	-
Reverse Phase C-18 on Chromosorb G	(C <sub>18</sub> H <sub>37</sub> SiO <sub>3</sub> /2) <sub>n</sub>	Not Available	-	-
Cyano on silica	SiRCN	Baker	-	-

Micropak MCH-10 and C-18 on Chromosorb-G are C-18 reverse phase packings, and are expected to be functionally equivalent. Micropak MCH-10 is a very fine material with a particle size of ~10 $\mu$  which could cause severe pumping problems in water sampling applications. There are several large mesh C-18 reverse phase packings commercially available.

Porapak R and N are vinyl pyrrolidone esters, and Porapak S is a vinyl pyridine ester. There is not much information available on the application of these resins to solid sorbent sampling, however the nitrogen heterocyclic functional group on these resins is expected to alter the sorbate-sorbent interaction.

*how? - to our benefit?*

Four sorbents have been specified in the contract for inclusion in the laboratory screening tests. They are:

Amberlite XAD-2

Ambersorb XE-340

Micropak MCH-10

Surface-bonded C<sub>18</sub> on Chromosorb G

Since surface bonded C<sub>18</sub> on Chromosorb G is not a commercially available sorbent, it would have to be custom synthesized at very high cost (Denboske, 1981). It is recommended that a commercially available product such as Baker extraction tubes or Waters SEP-PAK cartridges packed with surface-bonded C<sub>18</sub> on silica be used instead of C<sub>18</sub> on Chromosorb G. It is also recommended that Amberlite XAD-4 be substituted for XAD-2 because it is chemically similar to XAD-2, but has a larger surface area and therefore a higher capacity. Chromosorb 101 and 102, and Porapak P and Q are sufficiently similar to XAD-2 to be eliminated from further consideration.

*why so important?*

Of the remaining macroreticular sorbents, one resin should be chosen from each of the following groups whose members are functionally similar:

A. Vinyl pyrrolidones

1. Porapak N
2. Porapak R

B. Acrylic esters

1. Amberlite XAD-7
2. Amberlite XAD-8
3. Chromosorb 107



- 4. Chromosorb 108
- 5. Porapak T
- C. Acrylonitrile divinylbenzene
  - 1. Chromosorb 104
- D. Vinyl pyridine
  - 1. Porapak S

Since the three carbonaceous resins available differ so widely in their affinities for water, all three Ambersorbs will be included in the initial screening. Activated carbon and SEP-PAK or Baker Cyano cartridges will also be included in the screening studies.

Of the classes of sorbents examined, three were rejected on the basis of this literature search. Tenax GC will not be included in the screening experiments because of its low sorbate capacity and because of anticipated complications involved in its use with water. Polyurethane foam will not be included because of the poor recovery of organics reported in the literature. Alumina, silica gel and molecular sieves will not be included because of their high affinity for water.

A complete list of the sorbents proposed for the initial screening experiments is presented in Table XXII. While not all of these sorbents have been used for water sampling, a representative of nearly all of the sorbent classes discussed in this report is included. Sorbents were chosen so that screening tests could determine the effectiveness and possible applicability of each of these classes of sorbents to the recovery from water of the organics of interest.

TABLE XXII. Recommended Sorbents for Screening Experiments

✓ Amberlite XAD-4 -OK

✓ Porapak N or Porapak R -OK - ~~not chosen~~ prioritize

✓ Amberlite XAD-7, XAD-8, Chromosorb 107, 108, or Porapak T prioritize

✓ Chromosorb 104

✓ Porapak S -OK

✓ Ambersorb 340 -OK

✓ Ambersorb 347 -OK

✓ Ambersorb 348 -OK

✓ Micropak MCH-10 - delete! (particle size too small)

Activated Carbon -OK

✓ Baker or ~~Sep-Pak~~ Surface-Bonded C<sub>18</sub> on Silica Cartridges -OK

✓ Baker or ~~Sep-Pak~~ Cyano Cartridges -OK

prioritize 1, 3, or 6 ml sizes

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